

Photochemistry of organic nitrates studied using cavity ring-down spectroscopy

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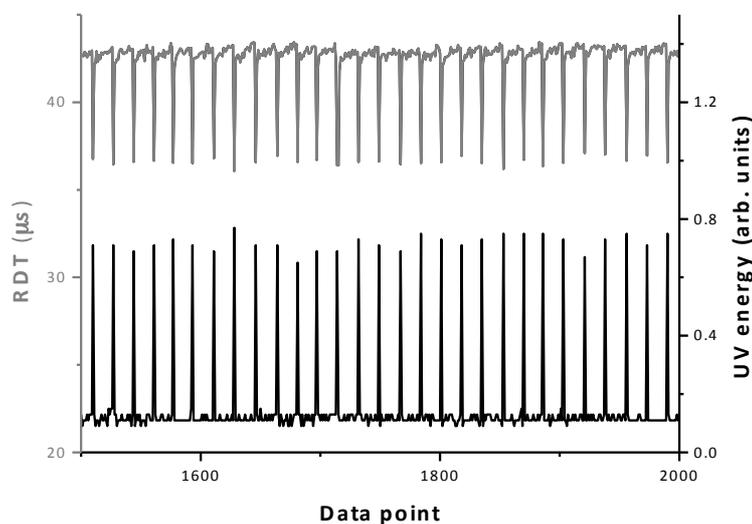
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Organic nitrates (RONO₂) are important trace species in atmospheric chemistry. They have the potential to act as temporary NO_x reservoirs, allowing for transportation of NO_x over large distances and affecting regional air chemistry.

RONO₂ compounds exhibit broad, unstructured UV absorption spectra that steeply decrease in cross section with increasing wavelength. The absorption spectra show an intense band at 190 – 220 nm, resulting from $\pi - \pi^*$ transitions. A weaker band, assigned to $n - \pi^*$ excitation extends to approximately 330 nm. It is this latter absorption that is responsible for tropospheric photolysis of RONO₂.

Absorption cross sections, NO₂ quantum yields and photolysis lifetimes have been measured for various RONO₂ compounds at tropospheric relevant ultraviolet wavelengths from 295 – 320 nm. Cavity ring-down spectroscopy has been used to detect NO₂ produced during RONO₂ photolysis. For isopropyl nitrate (C₃H₇ONO₂), at photolysis wavelengths of 295 and 315 nm, the NO₂ quantum yield has been found to be unity.



Typical experimental data for isopropyl nitrate (3.6 Torr partial pressure) at a photolysis wavelength of 295 nm (0.7 mJ/pulse).